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Temporal behavior of light-emission in the visible spectral range from a Ti–K_2CO_3–H cell

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Abstract

We report the generation of a hydrogen plasma and extreme ultraviolet emission as recorded via the hydrogen Balmer emission in the visible range. Typically, a hydrogen plasma is generated and the emission of extreme ultraviolet light from hydrogen gas is achieved via a discharge at high voltage, a high-power inductively coupled plasma, or a plasma created and heated to extreme temperatures by RF coupling (e.g. $> 10^6$ K) with confinement provided by a toroidal magnetic field. The observed plasma formed at low temperatures (e.g. $\approx 10^3$ K) from atomic hydrogen generated at a tungsten filament that heated a titanium dissociator coated with potassium carbonate. The temporal behavior of the plasma was recorded via hydrogen Balmer α line emission when all power into the cell was terminated. A 2 s decay of the plasma was observed after a fast decay of the electric field to zero. The persistence of emission following the removal of all of the power to the cell indicates that a novel chemical power source is present that forms an energetic plasma in hydrogen. No unusual behavior was observed with the control sodium carbonate. © 2000 International Association for Hydrogen Energy. Published by Elsevier Science Ltd. All rights reserved.

1. Introduction

A historical motivation to cause extreme ultraviolet (EUV) emission from a hydrogen gas was that the spectrum of hydrogen was first recorded from the only known source, the Sun [1]. Developed sources that provide a suitable intensity are high-voltage discharge, synchrotron, and inductively coupled plasma generators [2]. An important variant of the later type of source is a tokomak [3]. Fujimoto et al. [4] have determined the cross section for production of excited hydrogen atoms from the emission cross sections for Lyman and Balmer lines when molecular hydrogen is dissociated into excited atoms by electron collisions. This data was used to develop a collisional–radiative model to be used in determining the ratio of molecular-to-atomic hydrogen densities in tokomak plasmas. Their results indicate an excitation threshold of 17 eV for Lyman α emission. Addition of other gases would be expected to decrease the intensity of hydrogen lines which could be absorbed by the gas. Hollander and Wertheimer [5] found that within a selected range of parameters of a plasma created in a microwave resonator cavity, a hydrogen–oxygen plasma displays an emission that resembles the absorption of molecular oxygen. Whereas, a helium–hydrogen plasma emits a very intense hydrogen Lyman α radiation at 121.5 nm which is up to 40 times more intense than other lines in the spectrum. The Lyman α emission intensity showed a significant deviation from that predicted by the model of Fujimoto et al. [4] and from the emission of hydrogen alone.

We report that a hydrogen plasma is formed at low temperatures (e.g. $\approx 10^3$ K) by reaction of atomic hydrogen with potassium atoms, but not with sodium atoms. Atomic hydrogen was generated by dissociation at a tungsten filament and at a transition metal dissociator that was incandescently heated by the filament. Potassium metal formed by thermal decomposition of K_2CO_3 and by reaction with hydrogen. Potassium atoms were vaporized by heating to form a low vapor pressure (e.g. 1 Torr). The kinetic energy of the thermal electrons at the experimental

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temperature of $\approx 10^3$ K were about 0.1 eV, and the average collisional energies of electrons accelerated by the field of the filament were less than 1 eV. (No blackbody emission was recorded for wavelengths shorter than 400 nm.) Potassium atoms ionize at integer multiples of the potential energy of atomic hydrogen and caused hydrogen EUV emission; whereas, the chemically equivalent atom, sodium, caused no emission. Helium ions present in the experiment of Hollander and Wertheimer [5] ionize at a multiple of two times the potential energy of atomic hydrogen. The mechanism of EUV emission cannot be explained by the conventional chemistry of hydrogen, but it is predicted by a solution of the wave equation with a nonradiative boundary constraint put forward by Mills [6].

Mills predicts that certain atoms or ions serve as catalysts to release energy from hydrogen to produce an increased binding energy hydrogen atom called a *hydrino atom* having a binding energy of

$$\text{Binding Energy} = \frac{13.6\ \text{eV}}{n^2}, \tag{1}$$

where

$$n = \frac{1}{2}, \frac{1}{3}, \frac{1}{4}, \ldots, \frac{1}{p} \tag{2}$$

and p is an integer greater than 1, designated as $H[a_H/p]$ with a_H being the radius of the hydrogen atom. Hydrinos are predicted to form by reacting an ordinary hydrogen atom with a catalyst having a net enthalpy of reaction of about

$$m \cdot 27.2\ \text{eV}, \tag{3}$$

where m is an integer. This catalysis releases energy from the hydrogen atom with a commensurate decrease in size of the hydrogen atom, $r_n = na_H$. For example, the catalysis of $H(n=1)$ to $H(n=1/2)$ releases 40.8 eV, and the hydrogen radius decreases from a_H to $\frac{1}{2}a_H$.

The excited energy states of atomic hydrogen are also given by Eq. (1) except that

$$n = 1, 2, 3, \ldots. \tag{4}$$

The $n = 1$ state is the "ground" state for "pure" photon transitions (the $n = 1$ state can absorb a photon and go to an excited electronic state, but it cannot release a photon and go to a lower-energy electronic state). However, an electron transition from the ground state to a lower-energy state is possible by a nonradiative energy transfer such as multipole coupling or a resonant collision mechanism. These lower-energy states have fractional quantum numbers, $n = 1/\text{integer}$. Processes that occur without photons and that require collisions are common. For example, the exothermic chemical reaction of H + H to form H_2 does not occur with the emission of a photon. Rather, the reaction requires a collision with a third body, M, to remove the bond energy- $H + H + M \rightarrow H_2 + M^*$ [7]. The third body distributes the energy from the exothermic reaction, and the end result is the H_2 molecule and an increase in the temperature of the system. Some commercial phosphors are based on nonradiative energy transfer involving multipole coupling. For example, the strong absorption strength of Sb^{3+} ions along with the efficient nonradiative transfer of excitation from Sb^{3+} to Mn^{2+}, are responsible for the strong manganese luminescence from phosphors containing these ions [8]. Similarly, the $n = 1$ state of hydrogen and the $n = 1/\text{integer}$ states of hydrogen are nonradiative, but a transition between two nonradiative states is possible via a nonradiative energy transfer, say $n = 1 \text{–} \frac{1}{2}$. In these cases, during the transition the electron couples to another electron transition, electron transfer reaction, or inelastic scattering reaction which can absorb the exact amount of energy that must be removed from the hydrogen atom. Thus, a catalyst provides a net positive enthalpy of reaction of $m \cdot 27.2$ eV (i.e. it absorbs $m \cdot 27.2$ eV where m is an integer). Certain atoms or ions serve as catalysts which resonantly accept energy from hydrogen atoms and release the energy to the surroundings to effect electronic transitions to fractional quantum energy levels.

The catalysis of hydrogen involves the nonradiative transfer of energy from atomic hydrogen to a catalyst which may then release the transferred energy by radiative and nonradiative mechanisms. As a consequence of the nonradiative energy transfer, the hydrogen atom becomes unstable and emits further energy until it achieves a lower-energy nonradiative state having a principal energy level given by Eqs. (1) and (2).

The energy released during catalysis may undergo internal conversion and ionize or excite molecular and atomic hydrogen resulting in hydrogen emission which includes well characterized ultraviolet lines such as the Lyman series and the visible Balmer series. Balmer emission was sought by visible spectroscopy. The existence of Balmer emission requires that Lyman emission is also generated. This confirms that a hydrogen plasma exists. The temporal behavior of the light emission in the visible range was recorded when all of the power into the cell was removed. The persistence of visible emission when the field was zero was a means to determine whether the plasma was due to the externally applied power or whether a novel chemical source of power that required potassium and hydrogen was responsible.

2. Experimental

INP Greifswald, Germany recorded the temporal behavior of light-emission in the visible spectral range from a $Ti\text{–}K_2CO_3\text{–}H$ cell at the request of Black Light Power, Inc. of Cranbury, NJ, USA [9]. The quartz cell in the experimental set up, shown in Fig. 1, was provided by Black Light Power, Inc. Cranbury, NJ, USA. It comprised a quartz cell which was 500 mm in length and 50 mm in diameter. Two ports for gas inlet and outlet were on the end of the cell. A tungsten filament (0.5 mm, total resistance $\sim 2.5\ \Omega$) and a titanium or nickel cylindrical screen (300 mm long and 40 mm in diameter) that performed as a hydrogen

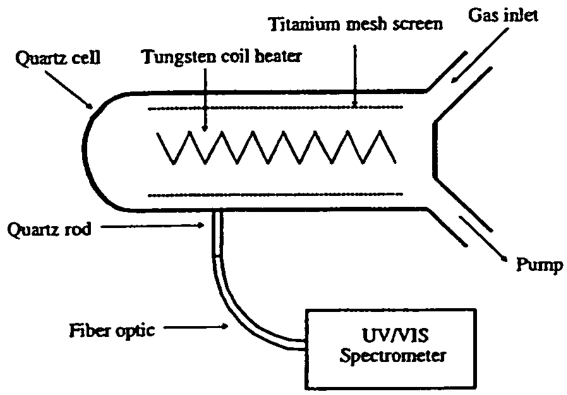

Fig. 1. Experimental setup for observing the UV/Vis spectrum and temporal behavior of light emission from a Ti–K_2CO_3–H cell.

dissociator were inside the quartz cell. The filament was 0.508 mm in diameter and 800 cm in length. The filament was coiled on a grooved ceramic support to maintain its shape when heated. The return lead ran through the middle of the ceramic support. The titanium screen was electrically floated. The power applied to the filament was 300 W and was supplied by a Sorensen 80-13 power supply which was controlled by a constant power controller. The voltage across the filament was about 55 V and the current was about 5.5 A at 300 W. The temperature of the tungsten filament was estimated to be in the range of 1100–1500°C. The external cell wall temperature was about 700°C. The hydrogen gas pressure inside the cell was maintained at about 500 mTorr. The entire quartz cell was enclosed inside an insulation package comprised of Zircar AL-30 insulation. Several K-type thermocouples were placed in the insulation to measure key temperatures of the cell and insulation. The thermocouples were read with a multichannel computer data acquisition system.

In the present study, the light-emission phenomena was studied for potassium carbonate and sodium carbonate. The inorganic test materials were coated on a titanium screen dissociator by the method of wet impregnation. That is the screen was coated by dipping it in a 0.6 M K_2CO_3/10% H_2O_2 or 0.6 M Na_2CO_3/10% H_2O_2 and the crystalline material was dried on the surface by heating for 12 h in a drying oven at 130°C. A new dissociator was used for each experiment. The alkali carbonates on the screen were heated by the tungsten filament with flowing hydrogen to form the corresponding alkali metal which vaporized.

The light emission was introduced to a UV/Vis monochromator for spectral measurement. The wavelength region covered by the monochromator was 380–720 nm. The UV/Vis spectrum (380–720 nm) of the cell emission was recorded with a photomultiplier tube (PMT) and a sodium salicylate scintillator.

The UV/Vis emission from the gas cell was channeled into the UV/Vis spectrometer using a fiber optic cable. The observation of the plasma in the cell was "side-on". The gap between the hot quartz wall of the cell and the glass cable was bridged by a quartz rod. The room was made dark. The other end of the fiber optic cable was fixed in an aperture manifold that attached to the entrance aperture of the UV/Vis spectrometer.

In order to study the temporal behavior of the cell, the current of the heater was interrupted by a commercial opener with an opening time of under 2 m which set the voltage to zero. The emission was filtered with an interference filter for the hydrogen Balmer alpha line (Model # λ_{max} = 652 nm; FWHM = 7 nm). The filtered emission was detected by a photomultiplier and recorded by a storing scope.

3. Results

Fig. 2 shows a spectrum recorded of a plasma that formed in the cell containing K_2CO_3. The atomic hydrogen Balmer series was observed such as Balmer α at 656 nm, Balmer β at 486 nm, and Balmer γ at 434 nm. Molecular hydrogen emission was also observed such as the Fulcher band in the region 580–650 nm as well as potassium lines. The light-emission occurred when the formation of potassium metal was noted by the formation of a mirror on the walls of the top of the cell. This occurred after the power of the filament was increased to above 300 W for about 10 min. The light was emitted for a period depending on the temperature (heater power level), and quantity of K_2CO_3 deposited on the titanium dissociator in the cell. Higher power would cause higher temperature and higher emission intensity, but a shorter duration of emission was observed in this case because the potassium metal formed and migrated from the cell more quickly under these conditions. The emission lasted from 20 min to 6 h depending on how much K_2CO_3 was initially present in the cell and the power level which corresponded to the cell temperature.

The dissociator was present in all experiments. Spectra were recorded under identical conditions wherein (1) K_2CO_3 was present without hydrogen, (2) only hydrogen was present, (3) K_2CO_3 was present and hydrogen was absent, and (4) Na_2CO_3 replaced K_2CO_3 and hydrogen was present. In these cases, only the blackbody radiation of the filament was observed.

The temporal behavior of the plasma was studied following the interruption and restoration of the power. Only the cell containing K_2CO_3 with hydrogen was studied since this was the only case in which a plasma was formed. The monochromator was adjusted to the range around 670 nm, a part of the spectrum where no line radiation was observed, and the blackbody radiation from the heater was significant. It took about 10 min, before plasma was observed in the cell. Then, the heater current was interrupted several times. The recorded radiation decayed with a time constant of about 2 s.

Next, the hydrogen Balmer α line was selected using an interference filter at a wavelength of 652 nm with a full-width at half-maximum of 7 nm. It was determined

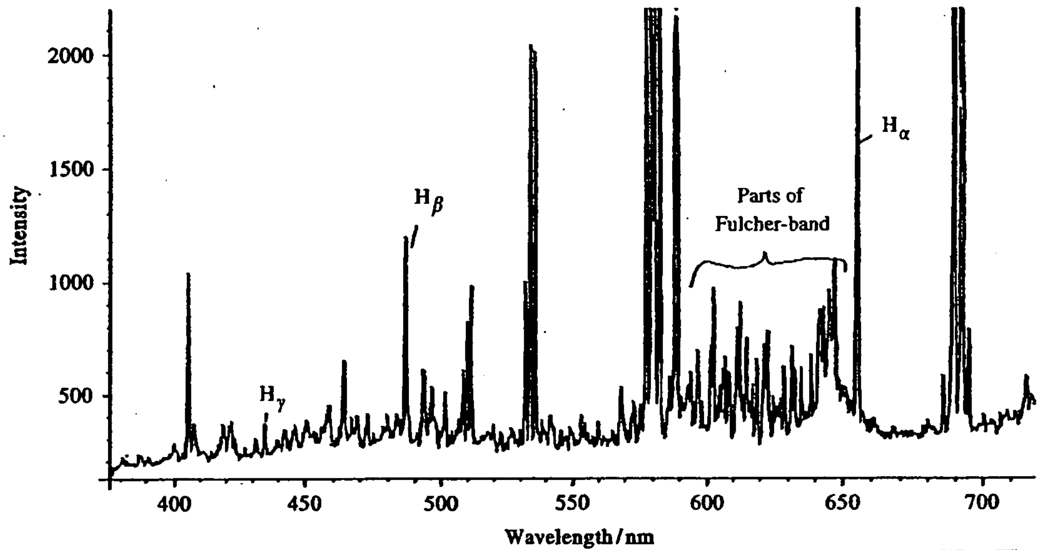

Fig. 2. A UV/Vis spectrum (380–720 nm) recorded of a plasma that formed in the cell containing K_2CO_3 after 30 min.

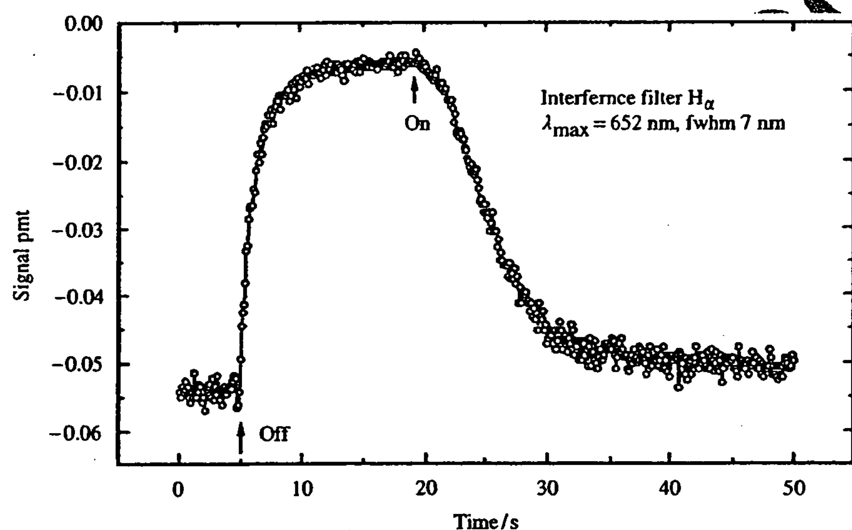

Fig. 3. The photomultiplier signal of the hydrogen Balmer α line displayed as a negative signal as a function of time while the heater power was switched off and on.

that the amplitude of the signal of the Balmer α line was orders of magnitude higher than the signal from the black-body light of the heater. The heater current was interrupted again several times with sufficient spacing between the interruptions, so that the line emission always returned to its previous level. The emission of the cell as a function of time while the heater power was turned off and on is shown in Fig. 3. The signal is displayed as negative. It returns to baseline as a function of time with interruption, and the opposite occurs with a longer time constant upon restoration of the heater power. The time constant of the decay of the hydrogen plasma following interruption of the heater power may be determined from the signal as a function of time which appears in Fig. 4. The time constant of the signal intensity change was about 2 s. The thermal decay of the filament was observed to have the same time constant.

4. Discussion

In the cases where plasma was observed, no possible chemical reactions of the tungsten filament, the titanium

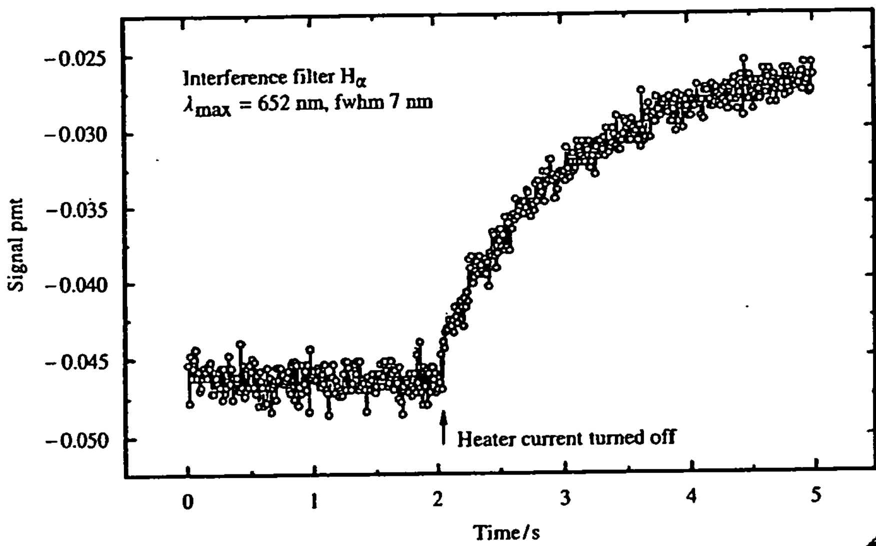

Fig. 4. The photomultiplier signal of the hydrogen Balmer α line displayed as a negative signal as a function of time after the heater power was switched off.

dissociator, potassium carbonate, and 300 mTorr hydrogen at a cell temperature of 700°C could be found which accounted for the plasma. In fact, no known chemical reaction releases enough energy to form a hydrogen plasma, and the reduction of K_2CO_3 by hydrogen is very endothermic. The dissociator was present in all experiments. The emission was not observed with the cell alone, with hydrogen alone, K_2CO_3 alone, or under identical conditions wherein Na_2CO_3 replaced K_2CO_3. No emission was observed until the cell temperature increased to a level that potassium metal was observed to form. Hydrogen line emission was occurring even though the voltage between the heater wires was set to and measured to be zero. These results indicate that the emission was due to a reaction of atomic hydrogen with potassium atoms.

According to Mills [6], a catalytic system is provided by the ionization of t electrons from an atom to a continuum energy level such that the sum of the ionization energies of the t electrons is approximately $m \times 27.2$ eV where m is an integer. One such catalytic system involves potassium. The first, second, and third ionization energies of potassium are 4.34066, 31.63, and 45.806 eV, respectively [10]. The triple ionization ($t = 3$) reaction of K to K^{3+}, then, has a net enthalpy of reaction of 81.7426 eV, which is equivalent to $m = 3$ in Eq. (3):

$$81.7426\ \text{eV} + K(m) + H\left[\frac{a_H}{p}\right] \to K^{3+} + 3e^- + H\left[\frac{a_H}{(p+3)}\right] + [(p+3)^2 - p^2] \times 13.6\ \text{eV}, \quad (5)$$

$$K^{3+} + 3e^- \to K(m) + 81.7426\ \text{eV}. \quad (6)$$

And, the overall reaction is

$$H\left[\frac{a_H}{p}\right] \to H\left[\frac{a_H}{(p+3)}\right] + [(p+3)^2 - p^2] \times 13.6\ \text{eV}. \quad (7)$$

No such reaction is possible for sodium.

When the power was interrupted, the hydrogen line emission decay matched the thermal decay of the filament. It may be attributed to chemical reactions because typically their rates are dependent on the temperature. Candidate chemical reactions are the hydrogen catalysis reaction, the dissociator of molecular hydrogen to atomic hydrogen, and the formation of potassium metal catalyst. (Atomic hydrogen and catalysts are required as reactants for hydrogen catalysis as given by Eqs. (5)–(7)).

Other studies support the possibility of a novel catalytic reaction of atomic hydrogen. It has been reported that intense EUV emission was observed at low temperatures (e.g. ≈ 10^3 K) from atomic hydrogen and certain atomized elements or certain gaseous ions which ionize at integer multiples of the potential energy of atomic hydrogen, 27.2 eV [11–16].

5. Conclusions

Line radiation from hydrogen emitted by the cell loaded with K_2CO_3 on titanium and operated in hydrogen requires a minimum temperature. The heat from the filament and possibly the weak dipole field from the filament may sustain the hydrogen plasma; but, it is not essential because hydrogen lines are emitted during times when this voltage is set to zero.

The emission from a plasma was observed at low temperatures (e.g. $\approx 10^3$ K) from atomic hydrogen and potassium atoms which ionize at integer multiples of the potential energy of atomic hydrogen. The release of energy from hydrogen was evidenced by the hydrogen Balmer emission which identifies EUV emission and the presence of a hydrogen plasma. The persistence of emission following the removal of all of the power to the cell indicates that novel chemical power source is present.

Novel compounds containing hydrino hydride ions have been isolated as products of the reaction of atomic hydrogen with potassium atoms and ions [17–23] identified as catalysts in a recent EUV studies [11–16]. The formation of novel compounds based on hydrino atoms is substantial evidence supporting catalysis of hydrogen as the mechanism of the observed EUV emission. The implications are that a vast new energy source and a new field of hydrogen chemistry have been discovered.

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